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ISOMERIZATION OF 1-BROMOPENTABORANE(9)  
BY BASE CATALYSIS <sup>1</sup>

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Sir:

The reversible conversion of 1-BrB<sub>5</sub>H<sub>8</sub> <sup>2</sup> to the previously

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(2) T. Onak and G. B. Dunks, Inorg. Chem., 3, 1060 (1964) and earlier references there cited.

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unknown and far more volatile isomer 2-BrB<sub>5</sub>H<sub>8</sub> is catalyzed by hexamethylenetetramine. Also effective is dimethyl ether, but with side reactions qualitatively varying with temperature; one result is a new synthesis of 1-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub>.

The relatively low volatility of 1-BrB<sub>5</sub>H<sub>8</sub> would relate to the negative charge at the apex of the B<sub>5</sub>H<sub>9</sub> skeleton; <sup>3</sup> and

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(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 110.

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and the enhanced B-Br bond polarity would gain effect from a probable molecular packing with the apex bromine atom near to the four basal boron atoms of another molecule. Such packing would be inconvenient for 2-BrB<sub>5</sub>H<sub>8</sub>. The CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> isomers show a smaller and opposite difference of volatility.

Syntheses. Direct Al<sub>2</sub>Cl<sub>6</sub>-catalyzed bromination of B<sub>5</sub>H<sub>9</sub> gave exclusively 1-BrB<sub>5</sub>H<sub>8</sub>, <sup>2</sup> but one experiment without any catalyst (12 hr., warming to 25°) gave a 4% fraction later recognized as 2-BrB<sub>5</sub>H<sub>8</sub>, with an 82% yield of 1-BrB<sub>5</sub>H<sub>8</sub>.

Isomerization. Freshly vacuum-sublimed (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (ca.

100 mg.) and 0.936 mmole of 1-BrB<sub>5</sub>H<sub>8</sub> (20 hr., sealed tube, 35°) gave 0.461 mmole of 1-BrB<sub>5</sub>H<sub>8</sub> and 0.454 mmole of far more volatile material having the same molecular weight (143.0 vs. 142.05 calcd.). Hydrolytic analysis of this gave 1.007Br<sup>-</sup>, 5.024B(OH)<sub>3</sub>, and 10.80H<sub>2</sub> per molecule. These results (and the absence of side reactions) prove the isomer.

Reversal of the isomerization was demonstrated by exposing 78 mg. of pure 2-BrB<sub>5</sub>H<sub>8</sub> to (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (18 hr., 24°). The yield of 1-BrB<sub>5</sub>H<sub>8</sub> was 12 mg. (15%) and the recovery of 2-BrB<sub>5</sub>H<sub>8</sub> was 65 mg. (83%).

Physical Properties. As indicated by the data of Tables I and II, the isomers could be separated easily by high-vacuum fractional condensation. Melting ranges: 36.5-36.7° for 1-BrB<sub>5</sub>H<sub>8</sub>; for 2-BrB<sub>5</sub>H<sub>8</sub>, -56.0 to -55.7°.

Table I. Volatility of Liquid 1-BrB<sub>5</sub>H<sub>8</sub>

$$(\log P = 5.0374 + 1.75 \log T - 0.0033T - 2420/T)$$

$$(t_{760} = 183.1^{\circ}; \text{ Trouton constant} = 20.9 \text{ e.u.})$$

Temp., °C.	36.5	45.9	50.8	56.0	61.8	70.0
<u>P</u> obsd, mm.	3.63	6.03	7.80	10.12	13.31	19.50
<u>P</u> calcd, mm.	3.63	6.05	7.79	10.11	13.37	19.50

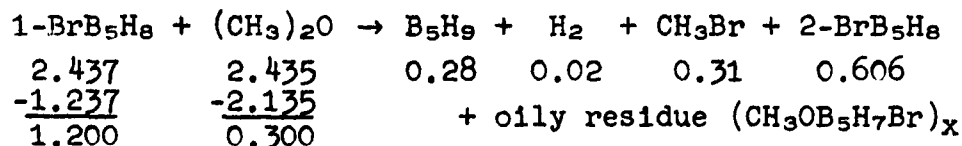
Table II. Volatility of Liquid 2-BrB<sub>5</sub>H<sub>8</sub>

$$(\log P = 5.8959 + 1.75 \log T - 0.0045T - 2367/T)$$

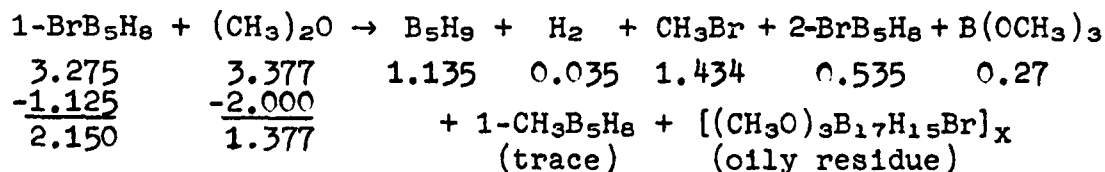
$$(t_{760} = 139.6^{\circ}; \text{ Trouton constant} = 21.16 \text{ e.u.})$$

Temp., °C.	17.80	30.85	34.45	38.50	52.75	59.60
<u>P</u> obsd, mm.	5.82	12.20	14.80	18.35	36.9	50.0
<u>P</u> calcd, mm.	5.80	12.24	14.82	18.31	36.7	50.0

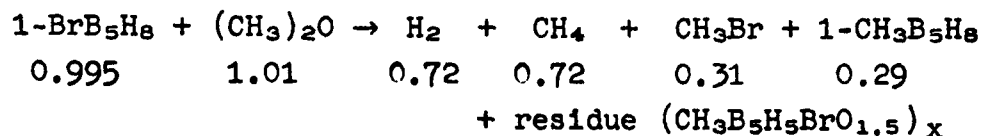
The Dimethyl Ether Reactions. A reaction occurring during 3 days at 0° can be summarized as follows, with stoichiometry in mmoles.



However, a 48-hr. run at 24° gave different results:



Then a 30-hr. process at 38° destroyed all BrB<sub>5</sub>H<sub>8</sub> but gave a fair yield of 1-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> (characteristic infrared peaks, 1225, 1229, and 1232 cm<sup>-1</sup>; no appearance of 2-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> peaks at 1106, 1111, and 1154 cm<sup>-1</sup>); stoichiometry:



Comparison of the latter two experiments suggests that B(OCH<sub>3</sub>)<sub>3</sub> served as a methylating agent. One may speculate whether the unknown CH<sub>3</sub>OB<sub>5</sub>H<sub>8</sub> was an unstable intermediate.

Methylpentaboranes. The (CH<sub>3</sub>)<sub>2</sub>O reactions yielded 1-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> but no 2-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub>; apparently catalysts were lacking. The isomerization is irreversible, as shown by full recovery of 2-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub> which had remained with 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N for 5 days at 27°— conditions causing complete conversion of 1-CH<sub>3</sub>B<sub>5</sub>H<sub>8</sub>.<sup>4</sup> This isomerization, when catalyzed in the vapor

(4) T. P. Onak, J. Am. Chem. Soc., 83, 2584 (1961)

phase by  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , does not depend upon transfer of  $\text{BH}_3$  groups, for only 4% of a sample of 1- $\text{CH}_3\text{B}_5\text{H}_8$  isomerized during a one-boron  $\text{B}^{10}\text{-B}^{11}$  exchange with  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$  at  $100^\circ$ . This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2- $\text{CH}_3\text{B}_5\text{H}_8$  (m.p.  $-55^\circ$ ),  $\log P = 6.889 + 1.75 \log T - 0.0065T - 2212/T$  (accuracy like Table II; example, 19.0 mm. at  $0^\circ$ ); thus it is roughly half as volatile as 1- $\text{CH}_3\text{B}_5\text{H}_8$  (34 mm. at  $0^\circ$ ).<sup>5</sup>

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(5) G. E. Ryschkewitsch et al., Inorg. Chem., 2, 891 (1963)

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Infrared Spectra. The infrared peaks shown in Table III were recorded accurately by the Beckman IR7 instrument. After each frequency ( $\text{cm}^{-1}$ ) the relative intensity  $k = (100/P)\log I_0/I$  (path 10 cm.; pressure P in mm.at  $25^\circ$ ) is given in parentheses. Assignments are omitted because they would be either obvious or controversial.

(Insert  
Table III  
p. 5)

Anton B. Burg, Jagtar S. Sandhu  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90007

Table III  
Infrared Spectra of Pentaborane Derivatives

1-BrB <sub>5</sub> H <sub>8</sub>	2-BrB <sub>5</sub> H <sub>8</sub>	1-CH <sub>3</sub> B <sub>5</sub> H <sub>8</sub>	2-CH <sub>3</sub> B <sub>5</sub> H <sub>8</sub>
. . . .	. . . .	2975(0.54)	2975(1.5)
. . . .	. . . .	2940(0.65)	. . . .
. . . .	. . . .	2931(2.5)	2930(0.86)
. . . .	. . . .	2862(1.3)	2861(0.32)
2622(7.6)	2622(7.2)	2600(19)	2600(19)
2480(0.36)	2500(0.41)	. . . .	2440(0.12)
. . . .	. . . .	1996(0.13)	1940(0.27)
1850(1.8)	1800(0.58)	1840(2.0)	1855(0.93)
1804(0.89)	1718(0.24)	1790(1.3)	1811(0.97)
1625R(0.91)	1625R(0.46)	. . . .	. . . .
1602Q(1.10)	1603Q(0.87)	1629(0.34)	1600(0.17)
1585P(0.56)	1584P(0.43)	. . . .	. . . .
1442(2.3)	1393(5.5)	1418(2.9)	1435(4.4)
1386(1.6)	1342(0.81)	1386(2.9)	1386(4.9)
. . . .	. . . .	1330R(0.82)	1330R(1.5)
. . . .	. . . .	1321Q(1.30)	1315Q(1.6)
. . . .	. . . .	1314P(0.46)	1310P(1.3)
. . . .	. . . .	1262(0.32)	. . . .
. . . .	. . . .	1232Q(2.1)	1154(1.4)
. . . .	. . . .	1229(1.9)	. . . .
1198(1.17)	. . . .	1225(1.8)	1111(0.65)
1152(2.5)	1120(0.93)	1168(0.20)	1106(0.68)
1065(0.82)	1029	1044R(0.28)	1036
1060(0.90)	1025(3.8)	1036Q(0.52)	1031(0.74)
1055(0.96)	1020	1026P(0.28)	1026
908(2.2)	887	907(5.9)	985(0.17)
861(1.1)	883(3.5)	. . . .	890(4.3)
. . . .	879	. . . .	. . . .
. . . .	856(1.55)	802(0.70)	. . . .
. . . .	. . . .	797(0.76)	. . . .
. . . .	. . . .	791(0.70)	. . . .
764	764	. . . .	. . . .
762(1.64)	762(0.63)	. . . .	. . . .
755	760	. . . .	. . . .
648(2.8)	639(2.9)	643(5.1)	643(2.8)



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